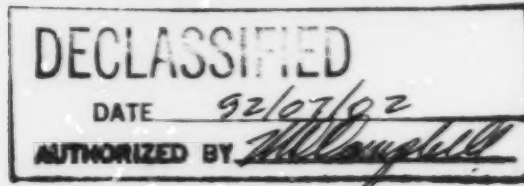


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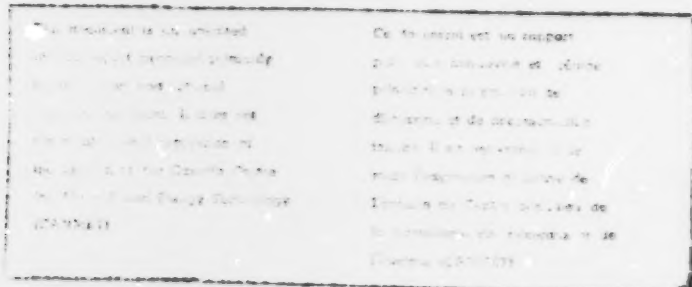


**STUDY METALS RECOVERY/RECYCLING
FROM ACID MINE DRAINAGE**

S U P P L E M E N T

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STUDY ON METALS RECOVERY/RECYCLING FROM ACID MINE DRAINAGE

S U P P L E M E N T

The literature review carried out in the main report revealed numerous processes to recover valuable metals from dilute acidic solutions. These processes should be evaluated for their applicability to AMD. There was a request to supplement the work by focusing on specific contaminants (i.e., Cu, Fe, Ni, Zn), critically assess the published techniques, offer specific recommendations and propose a focused research.

The criteria utilized in this supplemental evaluation were:

- the specific metals;
- economics;
- technical feasibility; and
- treated effluent quality.

BIOSORPTION OF METALS

CANMET has pilot plant data on the biosorption of uranium using immobilized Rhizopus arrhizus and has shown that a forty-fold concentration can be achieved with 100% recovery and that at least 16 loading/elution cycles can be achieved with the same biomass.

Current contract research at the University of Calgary has resulted in the isolation of indigenous bacteria from a nickel operation which preferentially bind nickel and cobalt with minimal binding of iron. Further studies are underway to determine the maximum loading capacity for nickel by immobilized biomass. If the results of the current study are encouraging, a pilot plant study should proceed. This may lead to a commercial process in 18-24 months.

Biosorption of other metals would require longer term research and commercial use would require a minimum of three to five years of research and process development. One would have to isolate bacteria or fungi that have a high specificity for a specific metal ion, low uptake of iron and that would adsorb metal ions at acidic to neutral pH's.

The targets in the development of this technology are: high metal specificity, high metal uptaking and low manufacturing costs, compared to metal selective resins. Selective nickel removal from AMD by immobilized biomass should be a research priority. Capital and operating costs are similar to those presented later in this Supplement for ion exchange technology. The benefits anticipated from the use of biosorption are associated with the development of a biomass significantly less expensive than the corresponding resin.

CHEMICAL TREATMENT

The chemical methods of interest to AMD treatment were presented in the main report and include:

- a) copper cementation with iron;
- b) selective iron removal; and
- c) metal removal/recovery (e.g., Ni, Zn).

a) Copper Cementation with Iron

CANMET investigations have shown that copper removal by cementation from dilute acidic solutions, such as AMD, is technically feasible. The critical question to be answered is: what is the lowest residual copper concentration in the treated effluent that can be achieved in a cost efficient manner?

Commercial copper cementation reactors have been designed to operate in concentrated solutions and are expected to have high operating costs in dilute solutions. There is an apparent need for new cementation reactors designed especially

for dilute solutions (i.e., AMD). In the specific case of Equity Silver Mines in B.C. lost copper value in AMD exceeds \$300,000 annually.

Order of magnitude capital and operating cost estimates (accuracy $\pm 40\%$) have been carried out by CANMET on a process to recover copper from a Mattabi Mine acid mine drainage. The copper cementation process was designed to treat a solution flow of 500 m³/h containing 0.5 g/L. This flow rate translates into 250 kg copper/h or 6 tonne copper/d. The cementation plant consisted of conventional cone type cementation vessels with 99% copper recovery. The estimated fixed capital cost is: **\$4,300,000**. The anticipated operating costs (**\$613,200/year**) will consist of iron replacement and pumping expenses. A copper precipitate will be produced which could be sent to a smelter or a refining operation. Although overall copper recovery costs should remain lower than the expected revenues, other benefits exist such as reduced sludge volume, reduced sludge contamination and improved sludge stability.

Investigations with a novel copper cementation reactor at CANMET have indicated that copper concentrations can be effectively reduced from 150 mg/L or higher to less than 5 mg/L. Copper is readily recovered in its metallic form with some iron contamination. The high costs to establish lower levels of copper concentration show that lime utilization is necessary to meet environmental standards. The initial ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in AMD will play an important role in iron consumption during copper cementation. Ferrous ion will be dissolved with cementation in AMD and it should be removed in a later stage.

Copper recovery by cementation with iron appears to be a very promising AMD treatment technology. Thus, it is proposed to proceed to bench scale studies that

involve the following areas:

a) **testing the new cementation reactor to:**

- improve cementation kinetics;
- decrease residual copper;
- minimize iron consumption and overall costs; and
- establish conditions for pilot plant design.

b) **comparison studies** between the new cementation reactor and a conventional precipitator.

c) **an economic evaluation** to establish a minimum acceptable copper concentration in AMD for copper recovery.

b) **Selective Iron Removal**

Iron is the most common metal contaminant in AMD in concentrations often exceeding 1.0 g/L. Iron removal takes place in any effluent neutralization methodology. High volume (1-2% solids) lime neutralization sludge is formed because of the polymerization of iron precipitates.

A well controlled ferrous to ferric oxidation and lime neutralization process will result in:

- complete iron removal;
- maximum sulphate removal;
- minimum heavy metal entrainment; and
- better precipitate quality.

The use of this precipitate for mine backfill appears possible, while other uses such as a material for road construction, pigments, etc. should be also examined.

Since iron removal from AMD by precipitation appears inevitable, research work to improve this treatment step is necessary. This research work should be directed towards:

i) **optimization of iron removal parameters**, such as:

- rate of ferrous oxidation;
- final solution pH;
- rate of lime addition;
- flocculation/coagulation schemes; and
- seeding materials.

ii) **by-product generation.**

Mineralogical analysis and surface chemistry investigations will enhance process chemistry understanding and efficient process development. Successful completion of this work will result in the elimination of the sludge disposal problem.

c) **Metal Removal/Recovery (Ni, Zn, ...)**

Iron removal from AMD results in solutions, containing residual heavy metals such as nickel and zinc. The method of metal recovery depends on the particular location and the final product use.

In the case of high metal concentrations, a metal hydroxide precipitate can be formed which will be recycled to a smelter. Increased gypsum and water contents are expected to be a liability. Further work on sludge volume, filterability and quality is necessary.

Capital and operating cost estimates ($\pm 40\%$) were carried out by CANMET with a Mattabi Mine acid mine drainage for a process to:

- recover copper by cementation with iron;
- neutralize acid with lime to pH 6 and precipitate iron and aluminum; and
- neutralize acid with lime to pH 11 and precipitate zinc, nickel and lead.

The process was designed to treat a solution flow of 500 m³/h having a pH of 2.2 and containing 0.5 g/L copper, 3.1 g/L zinc, 0.525 g/L aluminum, 0.00035 g/L nickel and 0.0027 g/L lead. The precipitated metal hydroxides are recovered in two settling ponds. Pond 1 contains iron and aluminum and pond 2 zinc, nickel and lead. In addition to the metal hydroxides both ponds will contain gypsum. The objective is to recycle sludge from the second pond to a nearby smelter.

The plant operates 24 h/d, 365 d/y, and is considered to be an addition to an existing complex, so that the cost of other external facilities and utilities are excluded. The estimated capital cost for neutralization and precipitation is **\$1,971,000** and the estimated operating cost is **\$4,584,000**, which translates to \$1.05/m³ soln. The large operating cost for neutralization and precipitation is due to the lime requirement, with 20% excess, 92 ton/d calcium oxide @ \$130/ton. Not included in the above operating costs is a charge for removal and disposal from the settling ponds of 108,000 ton/y of mixed gypsum and metal hydroxide precipitates. On a contract basis, this work could add \$200,000 to \$300,000 or more per year to the operating costs.

If metal pre-concentration is required to produce a usable solid product, then ion exchange or biosorption should be considered. These techniques will result in a highly purified effluent and a small volume of concentrated solution, which would be further processed.

ION EXCHANGE AND SOLVENT EXTRACTION

Ion exchange represents a potentially useful technique for the treatment of acid mine drainage waters. In particular, the following applications have the most potential:

1. **The selective extraction of heavy metals before neutralization.** The removal of heavy metals by adsorption rather than by precipitation reduces the environmental impact of the AMD solution. Some revenue may be generated depending on the nature and amount of metal to be recovered. The metals most amenable to this procedure are copper, nickel, cobalt and mercury.
2. **The removal of sulphate before neutralization.** This approach would have the following advantages: elimination of gypsum precipitation, easier recovery of metals, and improved quality of the effluent water. However, there may be several disadvantages. For example it requires a two-stage operation such as sulphate removal and effluent treatment and expected costs will be significantly higher than lime neutralization.
3. **The removal of soluble metals after neutralization.** According to normal practice, AMD solutions are neutralized to pH 9-10 to ensure the precipitation of the least basic metals such as zinc, lead and cadmium. The proposed approach would consist of neutralizing to pH 7 to precipitate iron and aluminum, followed by extraction of the soluble metals with ion exchange resins. A potential problem will be that of the co-precipitation of certain metals with the iron and gypsum. The control and mitigation of such co-precipitation must be further studied.

Solvent extraction can in principle be used for the same application as ion exchange. Solvent extraction offers better kinetics and selectivity, and it has favourable economics compared to ion exchange technology (see Table 1). However, there is a potential problem of organic entrainment in the effluent that should be treated.

Economical Aspects

Although ion exchange is generally considered to be expensive, the revenue from the recovered metals can offset to a large extent the operating costs. More importantly, ion

exchange offers important environmental benefits because the metals are recovered in a reusable form.

One of the major expenses is the cost of the resin itself. Modern selective resins cost about \$10-15 a litre. Thus, the capital cost of an IX plant tends to be significantly high. Capital cost estimates, similar to copper cementation estimates presented earlier, were performed at CANMET, for the selective recovery of copper with ion exchange. Solution flows of 500 m³/h with 0.5 g/L copper were used. The specified ion exchange resin had the following characteristics:

- load weight 20 kg copper/m³;
- adsorption time 1 to 2 h;
- resin cost \$15,000/m³.

The plant extracted 95% of the copper and consisted of one set of three columns, two absorbing with the third being eluted. The required bed volumes of resin were 4 at 250 m³ each. Based on these values, the estimated fixed capital costs were:

Ion exchange plant:	\$ 5,000,000
Resin @ \$15,000/m ³ :	<u>\$15,000,000</u>
Total fixed capital:	\$20,000,000.

These capital costs do not include installations for copper recovery from the eluates.

However, these resins have minimal attrition losses, particularly in dilute solutions such as AMD. The main operating expenses (\$2.5 M/year when EW is included) are the chemicals used for regeneration and resin replacement. In the case of AMD, the main chemical will be sulphuric acid.

Overall Research Plan

The following research program is proposed:

1. Select one or two typical AMD solutions.

2. Study the extraction of metals from the unmodified solution with various selective resins. The study would include elution from the resin and final recovery of valuable metals. The metals most likely to respond to this treatment would be copper, cobalt and nickel.
3. Evaluate the technical and economic aspects of this approach. Make recommendations about the continuation of the project.

The successful completion of this program could signal an interest to proceed with two other aspects:

1. Study the adsorption of residual metals from a solution neutralized to pH 7. The most likely metals to be found would be zinc, lead and cadmium.
2. Study the extraction of sulphate from the feed solution and determine its influence on the subsequent lime neutralization. Expected benefits: no gypsum, better metal precipitation and easier precipitate recovery, improved quality of the water (useful for industrial and domestic use). Anticipated disadvantages are: process complications and higher costs.

ELECTROWINNING

Electrowinning in concert with ion exchange offers the potential of recovering saleable metals from acid mine drainage solutions.

A high mass transfer (HMT) electrowinning cell may be used to electrowin **nickel** from the IX eluate. The pH would have to be adjusted and maintained at 3-4 during nickel electrowinning to prevent excessive hydrogen evolution.

HMT cell technology may be also employed to recover **zinc** cathode from the IX eluate. The spent electrolyte from the zinc electrowinning cell would be used for stripping the IX resin.

The costs incurred by electrowinning are significant. These costs can be significantly reduced by using smaller cathodes (say 2ft x 2ft), which could be removed by hand if necessary. Decreasing the anode-cathode separation will reduce the IR drop across the cell, thus reducing the energy consumption and improving agitation. It also reduces the size of the cell needed for a given cathode area requirement. The limiting current density for electrowinning is proportional to the metal concentration in the electrolyte. Concentration proportional current control, i.e., the current density is automatically varied on a real-time basis in proportion to the metal concentration, allows the cell to be operated as close as possible to the limiting current density at all times, thereby minimizing the capital costs.

Although selective electrowinning is a promising technology, a long-term research commitment is required to arrive to the desirable results. Canadian mineral industry needs a short to medium-term research for improvements to AMD treatment process.

PRELIMINARY COST ESTIMATES

Order of magnitude capital cost (accuracy $\pm 40\%$) and operating cost estimates have been prepared at CANMET for the recovery of copper from Mattabi Mine acid mine drainage solution by ion exchange-electrowinning (IX-EW), solvent extraction-electrowinning (SX-EW) and cementation processes. The processes were designed to treat a solution flow of 500 m³/h containing 0.5 g/L copper. This flow rate translates into 250 kg copper/h or 6 tonne copper/d. The plants operate 24 h/d, 350 d/y. The SX-EW and IX-EW plants recover 95% of the copper and copper cementation almost 100%. These plants are considered to be additions to existing complexes and the cost of other external facilities and utilities are excluded. The cost estimates

appear as follows:

Table 1. Preliminary Cost Estimates for the Recovery of Copper from a Mattabi AMD

Technology	Fixed Capital Cost (\$'000s)	Annual Operating Cost (\$'000s)
SX-EW	14,565	2,193
IX-EW	24,745	2,520
	(15,000 for resin inventory)	
Cementation	4,300	613

These cost estimates should be utilized with caution, since:

- conventional plant technology has been used, without a full appreciation of the AMD solution characteristics; and
- new cost efficient techniques have not been taken into account, due to lack of sufficient data.

Nevertheless, existing trends are apparent. These estimates are valid for copper recovery from Mattabi AMD, and extrapolation to other metal values should be avoided.

AMD TREATMENT PROCESS DEVELOPMENT

Detailed laboratory investigations should be carried out to study the recovery of metals, develop a treatment process flowsheet and evaluate the economic and environmental benefits. The need to establish a multi-disciplinary approach, where the previously discussed techniques are efficiently utilized, is obvious.

The research work is proposed to be structured in two stages: the first stage will be a short-term research resulting in a process flowsheet that can be readily applied in lime neutralization plants. The second stage will involve medium-term research leading to a sophisticated process flowsheet where alternative technologies are applied. Both of these stages are dependant to the solution characteristics and location of each AMD occurrence.

For the short-term stage, the process flowsheet will resemble the flowsheet in Figure 1. This schematic consists of several unit operations that involve:

- **copper removal** with conventional cementation reactors, producing a copper sludge to be recycled to a smelter;
- **iron precipitation** with oxidation of ferrous ion by aeration and partial solution neutralization, producing an iron sludge to be safely disposed; and
- **metals precipitation** by raising the solution pH and generating a sludge that can possibly be recycled to a smelter.

The drawbacks of this approach include larger sludge volumes, maintenance problems due to scaling and low value and quality of sludges produced. However, metal toxicity will be minimized and some revenue will be generated.

The process flowsheet generated by the medium-term research will be similar to the flowsheet in Figure 2. The main unit operations are as follows:

- **selective metal removal before neutralization**, that could involve:
 - copper cementation with a novel reactor,
 - copper removal with a selective resin,
 - nickel and cobalt removal with selective resins, if the solution characteristics are favourable, and
 - nickel and cobalt removal with selective biomass; and
- **selective iron removal**, with the utilization of improved precipitation techniques.

Finally, another unit operation should be investigated in the future, that is:

- **metal removal following neutralization**, with the use of ion exchange.

The need and feasibility of pre-concentration and polishing steps in AMD treatment will be evaluated in a later stage.

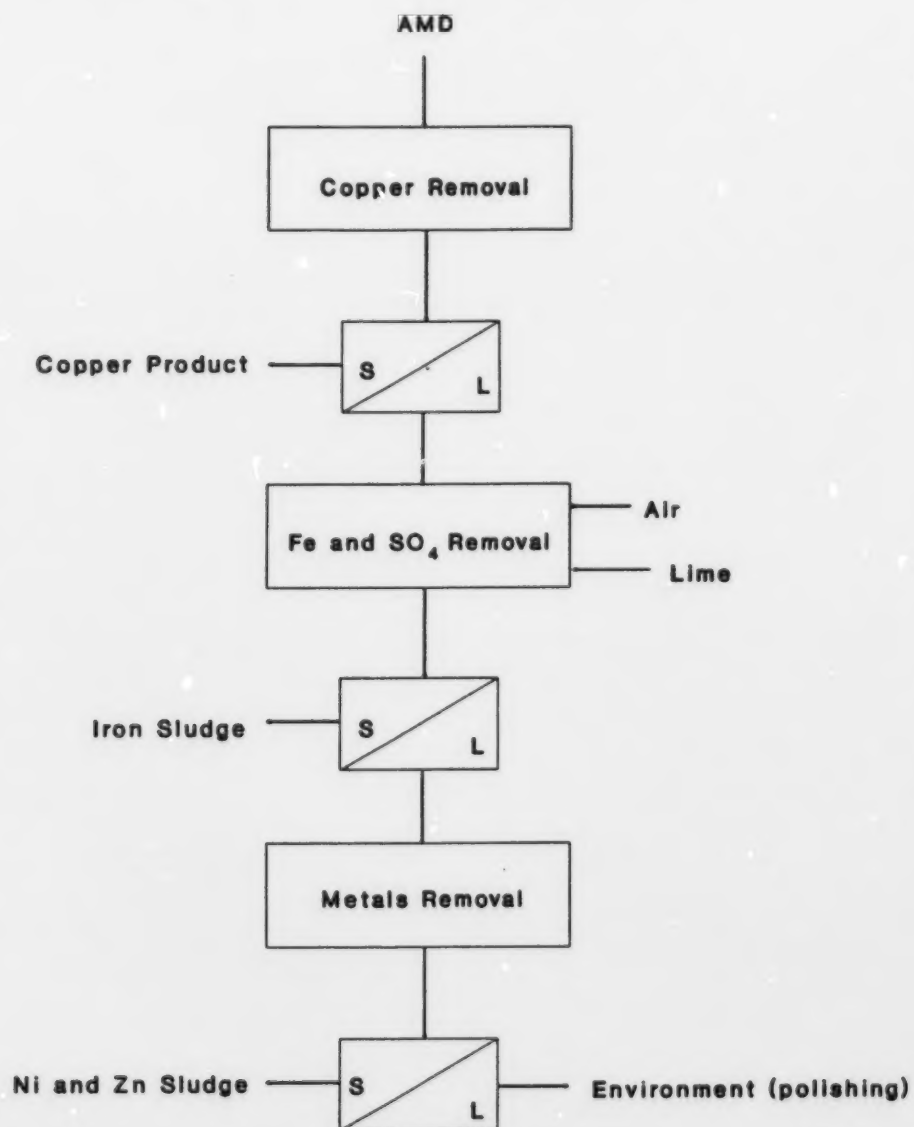


Figure 1: Potential AMD treatment process schematic.
(Short-term approach: 3-6 months research)

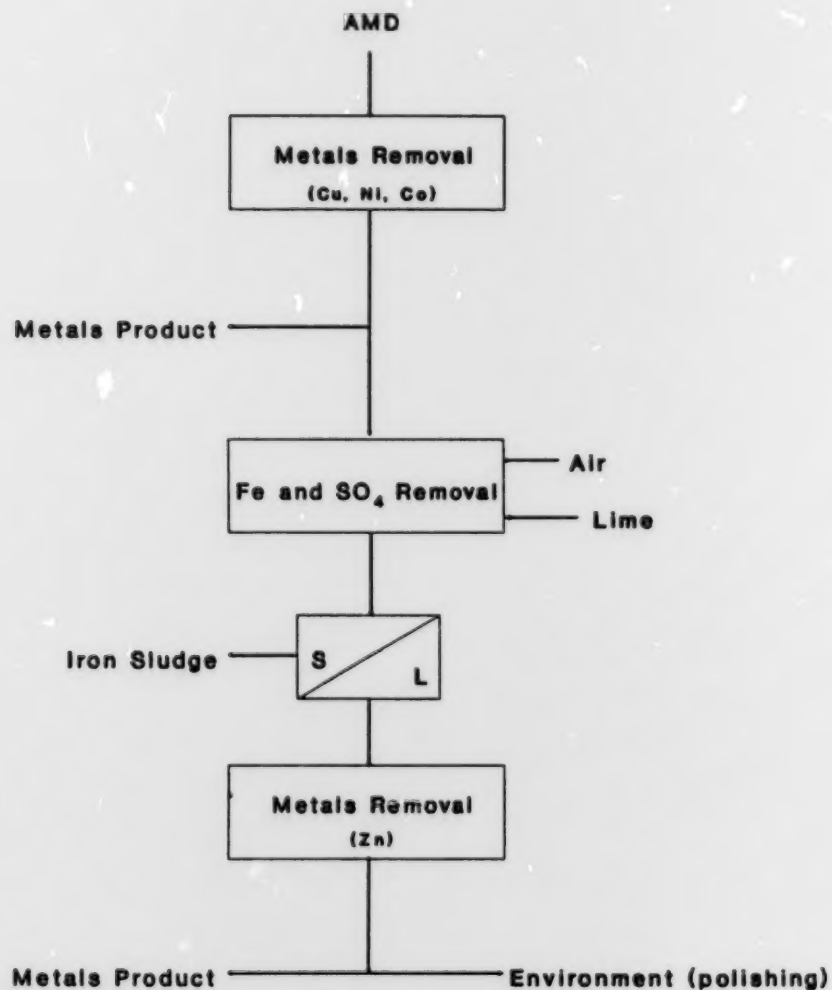


Figure 2: Potential AMD treatment process schematic.
(Medium term approach: 1-3 years research)